5.1.3. Low Electron Attachment Potential Species (LEAPS)

Measurements of halons H-1301 and H-1211, CFC-113, CH_3Br, and CH_3Cl continued with the new LEAPS GC system throughout 1993. Except for H-1301, these compounds were also measured by GC-MS throughout the year. Halon data from the EC-GC installed in April 1992 are extremely precise (within 0.01-0.03 ppt on average), although the response for H-1211 is still non-linear on the new system. By mid-1992, the data suggested a substantial slowdown in the growth of the two halons in the atmosphere [*Butler et al.*, 1992]. However, the recent values, which are more frequent and more precise and that extend the data set from 5 to 7 years, indicate that the slowdown may not be as substantial as previously reported. During 1993, atmospheric H-1211 increased at 0.1-0.2 ppt yr^{-1} (3-7% yr^{-1}), and H-1301 increased at about 0.2 ppt yr^{-1} (10% yr^{-1}). At the end of 1993, the latitudinally weighted, mean mole fractions of H-1301 and H-1211 are 2.1 and 3.1 ppt, representing 25-35% of organic bromine in the remote atmosphere (Figure 5.6).

Because of a numerical error in the calculation routines, previously reported values for H-1211 should be adjusted upward by 15%. Reanalyses of cylinder SRL-K-009288, an Aculife-treated steel cylinder that has served as the principal secondary standard for all reported halon values, have agreed within ±0.2 ppt for each of the halons over 3-5 years. Earlier calibrations, however, were not as precise as those done since early 1992, therefore it is difficult at this time to determine drift within this range. Data from the GC-MS and EC-GC systems agree within ±0.1 ppt overall.

One indicator of potential sampling error or storage effects is a comparison of agreement for flask pairs versus that for individual measurements of the same flask. From purely statistical considerations, one would expect flask-pair agreement to be better than the precision for individual measurements if there is no flask or sampling effect. This is because the value obtained for each flask is a mean and, consequently, a closer estimate of the true mean than is an individual measurement. From EC-GC measurements, it is clear that agreement for H-1301 within pairs of simultaneously collected flasks is similar to the analytical precision for repeat measurement of individual flasks (Figure 5.7*a*). Because surface effects in all flasks are not expected to be identical, this indicates that there is little chance of storage having affected H-1301. The median standard deviations for replicate analyses and for flask-pair agreement are both around ±0.01 ppt (±0.5%). (±1.3%). This is not a large effect and it may be symptomatic of some problem occurring within a flask after it has been sampled.

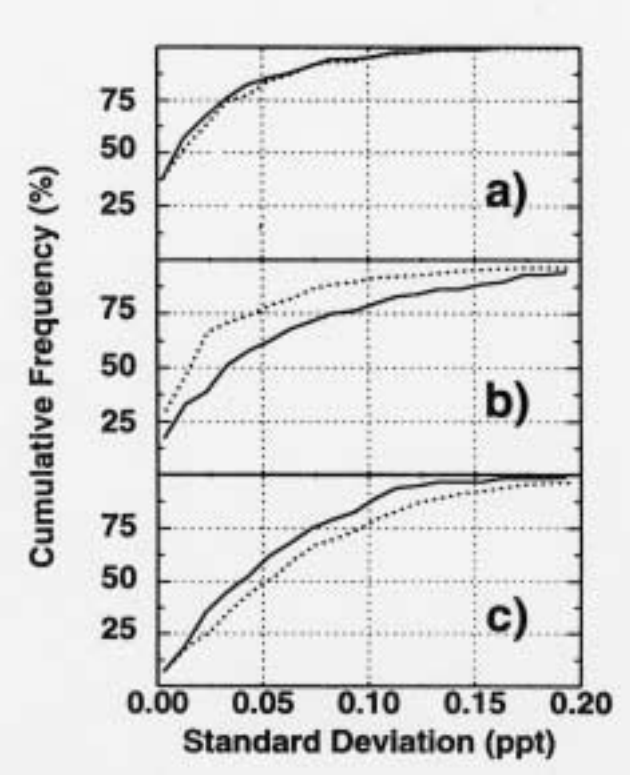

Fig. 5.6. Composite plots of all CMDL halon data (a) H-1301 (b) H-1211. Circles represent analyses with the old EC-GC, triangles represent analyses with the new EC-GC, squares are for data obtained by GC-MS (H-1211 only).

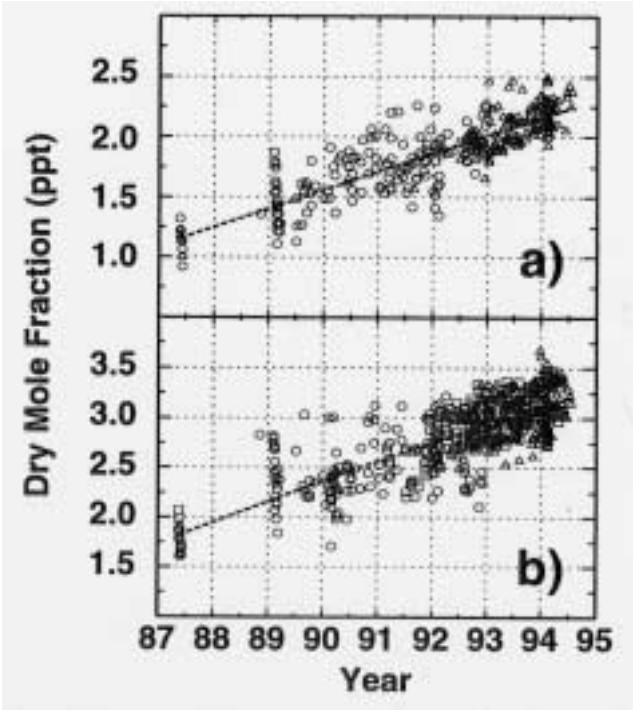

Fig. 5.7. Cumulative error plots for repeat analysis of individual flasks (dotted line) and analysis of flask pairs (solid line): (a) H-1301 by EC-GC, (b) H-1211 by EC-GC, (c) H-1211 by GC-MS.

However, for H-1211, agreement between flasks is somewhat poorer than for replicate analyses (Figure 5.7*b*). The median standard deviation for replicate analyses is ±0.02 ppt (±0.7%), but for flask pairs is ±0.04 ppt Whether this effect involves H-1211 directly or some other compound affecting the analysis is uncertain at this time. It does not appear related to sampling site, sampling dates, or time between sampling and analysis. The possibility that it may be something other than H-1211 is underscored by a similar evaluation for GC-MS data. In this case, the agreement for H-1211 between flasks is actually slightly better than that for replicate analyses, as one would expect from purely statistical considerations (Figure 5.7*c*). Because the GC-MS is specific for the m/z = +85 ion from H-1211 and the ECD is less specific, it is more probable that the larger differences between flask pairs, as observed by EC-GC, may be some matrix effect, such as that caused by a co-eluting compound. It is also possible, however, that the effect is just beyond the detection ability of the GC-MS.